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THE TRANSFORMATION OF ALKENES INTO γ-LACTONES USING α-IODOESTERS

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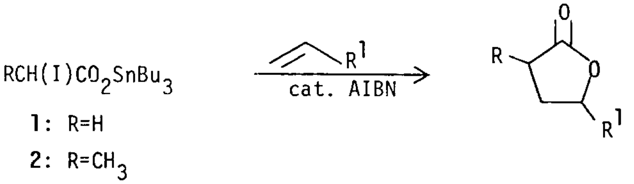
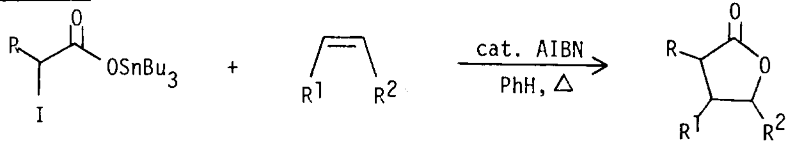
Summary: Iodostannyl esters react with alkenes in the presence of AIBN to afford γ-lactones.

Recently, the synthetic applications of free radical chemistry have increased dramatically. Building upon the foundations laid by Julia,[1] Beckwith[2] and others,[3] many carbon-carbon bond-forming reactions have been developed. Notable contributions include the vinyl radical cyclizations developed by Stork,[4] the allyl tin chemistry studied by Keck[5] and the formations of radicals from mercurials investigated by Giese[6] and others.[7] Heiba and Dessun[8] and, more recently, Fristad[9] have examined the reactions of acids with alkenes for the formation of lactones. The reaction requires the use of the highly reactive manganic triacetate and must be conducted under acidic conditions. In connection with our interest in furobenzofurans[10] we sought an olefin to lactone transformation which could be performed under neutral conditions. Our research has led to the novel transformation depicted below.



The stannyl esters 1 and 2 were easily made from inexpensive bis(tri-n-butyltin)oxide and the corresponding iodo acid.[11] While the bromo acids afforded stannyl esters equally well, the yields of the lactone formation reactions were higher when their iodo counterparts were used. Several initiation procedures were studied. Although a catalytic amount of tri-n-butyltin hydride was effective, photochemical initiations led to the formation of several byproducts. A catalytic amount of AIBN in refluxing benzene is an effective and convenient initiation procedure. The results of our study are illustrated in Table I.

Table I. The Synthesis of Lactones from Stannyl Esters



Entry	R	R^1	R^2	% Yield[a,c,d]
1	H	H	Bu	76
2	H	CH_2CH_2O		78
3	H	H	Oct	76
4	H	H	CH_2SiMe_3	56
5	H	H	OEt	36[b]
6	H	H	CH_2OH	73
7	H	H	CO_2Et	--
8	CH_3	H	Bu	75
9	CH_3	CH_2CH_2O		72

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[a] Yield after chromatography. All compounds exhibited ^{1}H NMR, IR and mass spec or analysis consistent with their assigned structures.

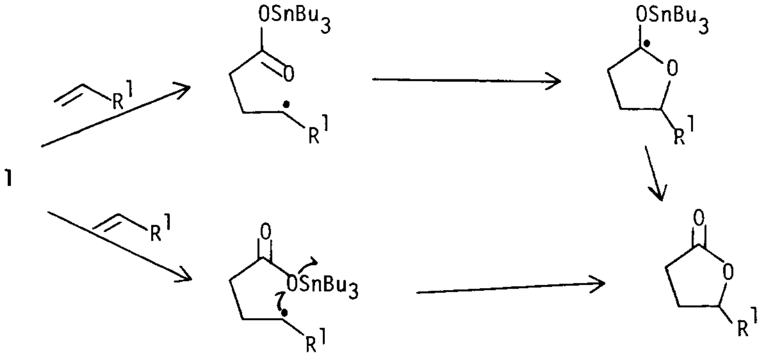
[b] An equal amount of an unidentified byproduct was formed.

[c] In a typical reaction, one equivalent of the iodoester, three equivalents of the alkene and 5 mole percent of AIBN were refluxed in benzene (1 M) for 8 h. After partition between acetonitrile and hexanes, the crude product was isolated.

[d] The lactone produced in entry 2 has a cis ring juncture as shown by 300 MHz NMR. The lactones in entries 8 and 9 are approximately a 50:50 mixture of diastercomers.

The effective cyclizations with electron-rich alkenes and the failure of the reaction with electron deficient alkenes[12] are consistent with the reaction profile of an electrophilic radical. The low yield obtained in the reaction with ethyl vinyl ether (entry 5) is due to the instability of the γ-ethoxybutyrolactone under the reaction conditions. Notably, hydrogen atom abstraction to form stabilized allylic radicals does not seem to compete with the cyclization reaction (entries 4 and 6).

The lactone formation reaction could proceed by either of the two pathways shown below. One mechanism involves cyclization to an acetal radical followed by loss of the



tri-n-butylstannyl radical. The other mechanism features an S_Hi reaction. The cyclization to form the acetal radical appears to violate Baldwin's rules.[13] However, the results of both Beckwith and Perkins concerning the mechanism of acetate transfer in β-acetoxyradicals provide a viable mechanistic alternative[14].

Lactones are important subunits in many natural products and serve as valuable building blocks for complex compounds. This reaction offers a useful alternative to existing ones. The advantages of mild reaction conditions and compatibility with a variety of functional groups should make this lactone formation reaction a versatile one.

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References and Notes

1. M. Julia Pure Appl. Chem., **1974**, 40, 553. M. Julia Acc. Chem. Res., **1971**, 4, 386.
2. A.L.J. Beckwith Aust. J. Chem., **1983**, 36, 545 and references therein.
3. For a comprehensive review, see J.-M. Surzer Reactive Intermediates, R. A. Abramovitch, ed. (Plenum Press, New York, 1982) Volume 2, 121. See also D. J. Hart Science, **1984**, 223, 883.
4. G. Stork, P. M. Sher J. Am. Chem. Soc., **1983**, 105, 6765 and references therein.
5. G. E. Keck, J. B. Yates J. Am. Chem. Soc., **1982**, 104, 5829.
6. B. Giese Angewandte Chemie Int. Ed., **1983**, 22, 753.
7. S. Danishefsky, E. Taniyama, R. R. Webb Tet. Lett., **1983**, 24, 11, 15. A. P. Kozikowski, J. Scripko Tet. Lett., **1983**, 2051.
8. E. I. Heiba, R. M. Dessau, W. J. Koehl J. Am. Chem. Soc., **1968**, 90, 5905. Ibid, **1969**, 91, 138.
9. W. E. Fristad, J. R. Peterson J. Org. Chem., submitted.
10. G. A. Kraus, J. O. Nagy, J. Delano Tet., submitted.
11. R. K. Ingham, S. D. Rosenberg, H. Gilman Chem. Rev., **1960**, 60, 459.
12. Acrylonitrile and ethyl cinnamate also failed to afford lactones.
13. J. E. Baldwin, L. I. Kruse J.C.S. Chem. Comm., **1977**, 233.
14. A. L. J. Beckwith, C. B. Thomas J.C.S. Perkin II, **1973**, 861, M. J. Perkins, B. P. Roberts J.C.S. Perkin II, **1975**, 77.

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